Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion **Anode Systems**

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Project ID #: ES061

Overview

Timeline

- Start: Jan 2013
- Finish: December 2013
- 100% complete

Budget

- Total project funding
 - \$1,182.7K
- Funding received in FY11
 - \$310.33K
- Funding for FY12
 - \$330.8K
- Funding for FY 13
 - \$330.8K
- Funding for FY 14
 - \$210.77K

Barriers

- <u>Performance</u>: Low specific energy and energy density, poor rate capability
- Life: Poor cycle life and coulombic efficiency
- Cost: High cost of raw materials and materials processing

Targets for PHEV (2015)

- > Available Energy: 3.5-11.6 kWh
- > Cycle life: 3,000-5,000 deep discharge
- > Recharge rate: 1.4-2.8 kW

Partners/Collaborators/Students

- Industries
 - Ford Motor Company

National Laboratory

- Dr. A. Manivannan, NETL
- · Dr. Vincent Battaglia, LBNL

Other Universities

- Dr. Spandan Maiti, University of Pittsburgh
- Dr. Shawn Litster, Carnegie Mellon University
- · Dr. Amit Acharya, Carnegie Mellon University
- Dr. Damodaran Krishnan, University of Pittsburgh

Research Faculty/Students

- · Dr. Moni Kanchan Datta, Univ. of Pittsburgh
- Dr. Oleg Velikokhatnyi, Univ. of Pittsburgh
- · Rigved Epur, Univ. of Pittsburgh
- · Bharat Gattu, Univ. of Pittsburgh
- · Karan Kadakia, Univ. of Pittsburgh
- · Prasad Patel, Univ. of Pittsburgh
- · Prashanth H. Jampani, Univ. of Pittsburgh
- Dr. Ramalinga Kuruba, Univ. of Pittsburgh
- · Sameer Damle, Univ. of Pittsburgh
- · Dr. Siladitya Pal, Univ. of Pittsburgh
- · Dr. Partha Saha, Univ. of Pittsburgh

Relevance Slide

Relevance/Objectives of this Study: March 2013-March 2014

- Identify new alternative nanostructured anode materials to replace synthetic graphite that will provide higher gravimetric and volumetric energy density
- Similar or lower irreversible loss (≤15%) in comparison to synthetic graphite
- Similar or better coulombic efficiency (≥99.95%) in comparison to synthetic graphite
- Similar or better cyclability and calendar life in comparison to synthetic graphite
- Investigate Microcrystalline (μm-Si), Nano-crystalline (nc-Si), Nanoparticle (np-Si), Nanowire and Nanotube (h-SiNT), and amorphous Si (a-Si) based nanocomposite anodes
- Improve the specific capacity, available energy density, rate capability, calendar life and cycle life of nano-structured and amorphous Si based anode materials
- Identify new water soluble natural source elastomeric thermoplastic binders capable of binding the active materials preventing de-lamination

Milestone Slide

Project Milestones

Month/Year	Milestones or Go/No-Go Decision
March 2013	Demonstrated scalable synthesis of hollow silicon nanotubes (h-SiNTs) using sacrificial inorganic nanowire template showing capacities >2000 mAh/g (completed)
June 2013	Cycling results on Si/C composite with the identified novel high strength water soluble binder (PP, PE and composite) indicate better capacity retention than commercial PVDF binder (completed)
September 2013	h-SiNTs with optimized morphology exhibited capacities >1000 mAh/g and excellent capacity retention (<0.067% loss per cycle, 400 cycles) (completed)
December 2013	h-SiNTs show good rate capability delivering capacities around 1500 mAh/g at high current rates (4A/g) (completed)

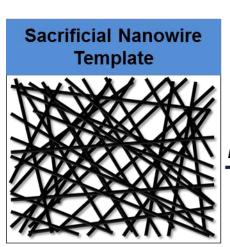
Si: Silicon, C: Graphite or Carbon, CNT: Carbon nanotube

Approach Slide

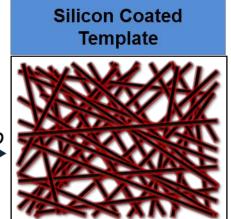
Approach/Strategies

- Explore Si, carbon/CNT, h-SiNT and a-Si film based nanocomposite anode
 - Explore <u>novel low cost approaches</u> to generate **hollow Silicon nanotubes (h-SiNTs)**, Si/C and Si/CNT composite comprising microcrystalline (μm-Si), nanocrystalline (nc-Si), nanoparticle (np-Si) or amorphous Si (a-Si) and a variety of carbon precursors:
 - · Electro-deposition
 - Chemical vapor deposition (CVD)
 - High energy mechanical milling (HEMM)
 - · Hydrothermal synthesis
 - Fluidized bed reactor (FBR)
- Explore interface control agents (ICA) to improve cyclability and coloumbic efficiency in CNT/Si based heterostructres
- Explore suitable surface control additives (SCA) and surface electron conducting additives (SECA) in Si/C nanocomposite which will reduce 1st cycle irreversible loss (FIR) and improve the coulombic efficiency (CE) in subsequent cycles
 - Coating of Si/C composite with suitable element or compound surface control additives (SCA) to improve CE and cycling stability.
 - Use of highly conductive additives to improve CE.
- Explore high strength, high ductility natural source elastomeric binders to bind the active materials
- Full cell and long cycling tests:
 - · Coin cell and pouch cell configuration with suitable cathode

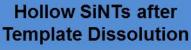
Large Scale Synthesis of Hollow Silicon Nanotubes (h-SiNTs)

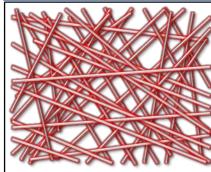


Si coating on network by CVD

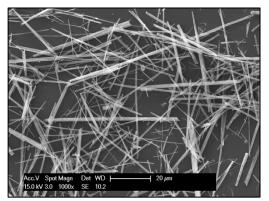


Leach template



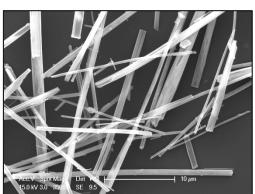




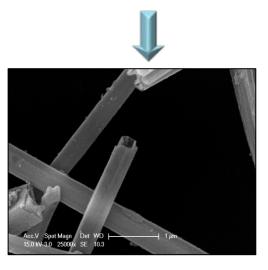


Diameters: 0.6-1 μmLength: 5-100 μm



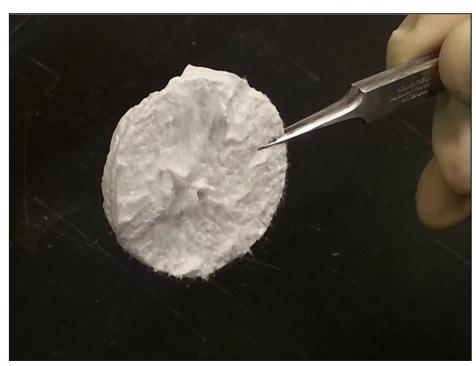


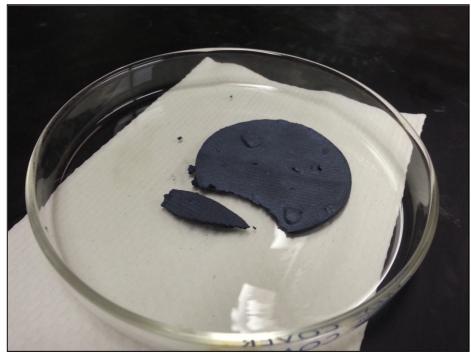
- Si coats uniformly on the template
- Forms a core shell (Si) morphology
- Si coating thickness: 60-80 nm



Hollow Silicon Nanotubes (h-SiNTs)

Inorganic Nanowire Template and h-SiNT Cake

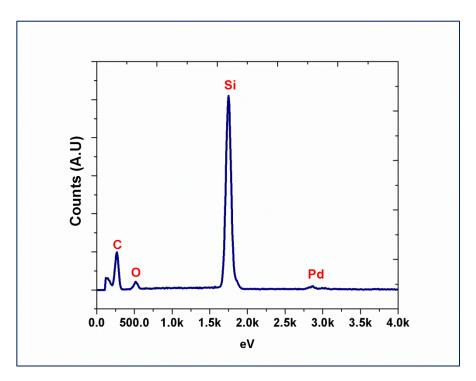


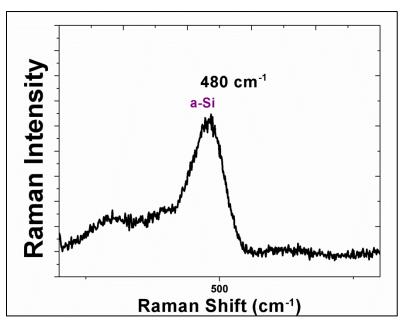


Sacrificial Inorganic Nanowire Template Cake

Hollow Si Nanotube Cake

EDAX and Raman Spectra

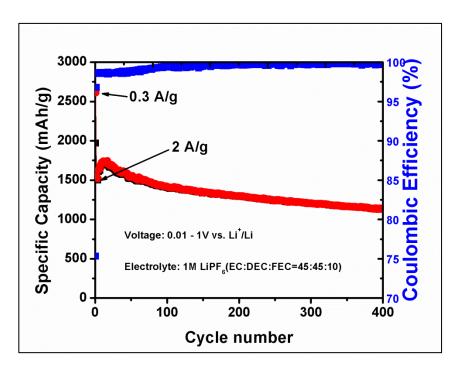


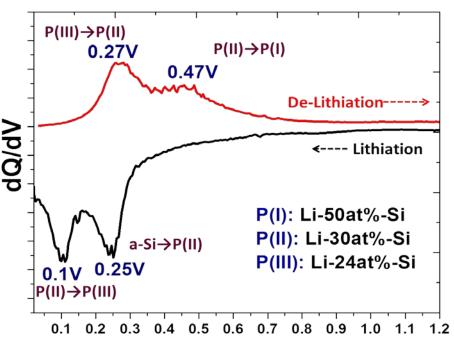


Element	Weight %	At %
СК	51.07	70.44
ОК	4.14	4.28
Si K	42.11	24.84

➤ Raman spectra shows the presence of Transverse Optical band (~480cm⁻¹) for amorphous Silicon

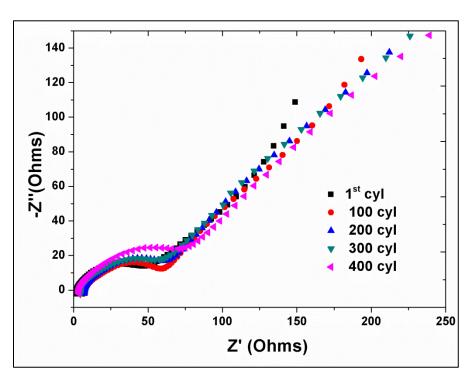
h-SiNTs: Electrochemical Characterization

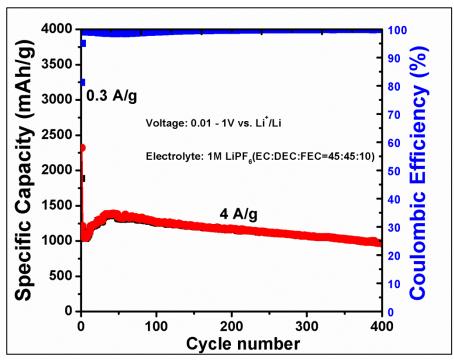




- ➤ Lithiation potential corresponds to reaction with a-Si (~0.25V and ~0.1V)
- ➤ High capacity (~2615 mAh/g) at high current rate (2A/g, ~1C)
- > IR loss: 25%, Coulombic Efficiency: 99.9%
- ➢ Good cyclability: 0.067% loss/cycle (400 cycles)
- Loading: 0.676 mg/cm²
- Capable of making slurries for large scale coating of current collectors

h-SiNTs: EIS Studies with Cycling

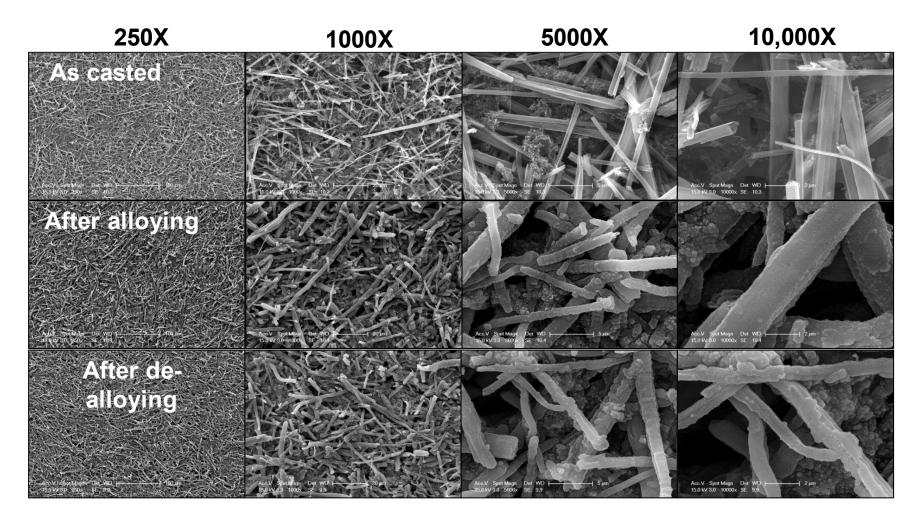




- AC bias=0V
- Amplitude: 10mV
- Frequency range=0.1 to 300,000 Hz
- After 1st cycle, the R_{ct} value remains invariant with number of cycles

- Capacities ~1000 mAh/g attained at high current rates (4A/g, 5C)
- Fade rate = 0.052% loss/cycle (400 cycles)
- Loading = 0.802 mg/cm²
- FIR = 19.5%

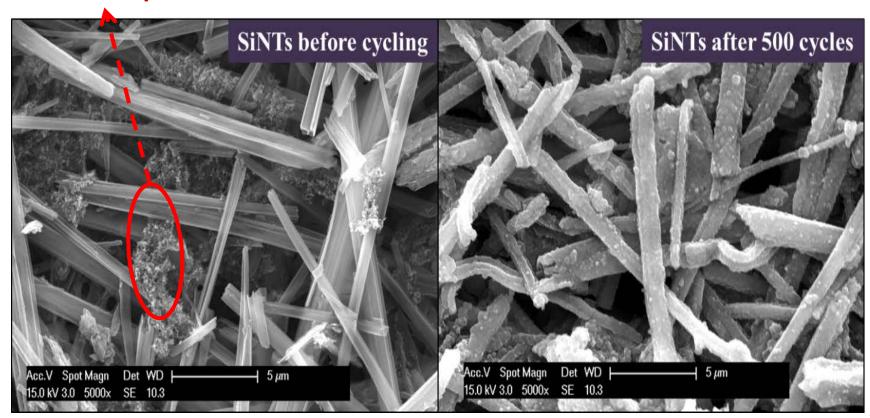
h-SiNTs: SEM after first cycle alloying & de-alloying



- > An increase in nanotube dimensions can be observed after lithiation due to volume expansion of Si
- After de-lithiation, nanotube structure remains intact without fracture along with volume contraction 11

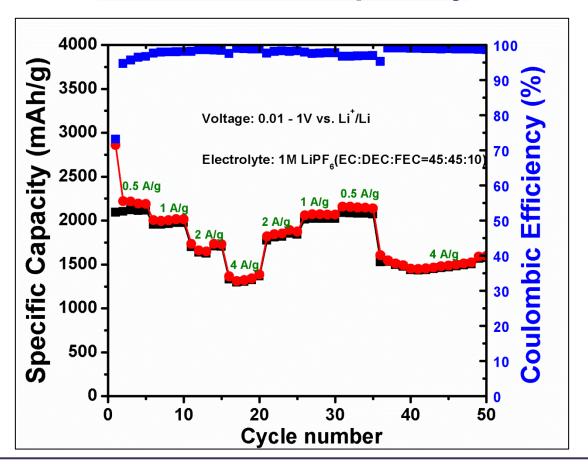
h-SiNTs: SEM before and after cycling (500 cycles)

Binder & Super-P



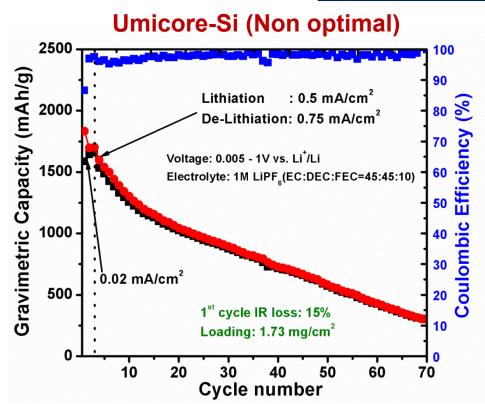
- ✓ Cycled at 4A/g between 0.01 1 V vs. Li⁺/Li
- ✓ The I-D nature of the SiNT still remains intact
- ✓ SEI seems to be present and coated uniformly onto the SiNTs
- Hollow structure will be analyzed by HRTEM

h-SiNTs: Rate Capability

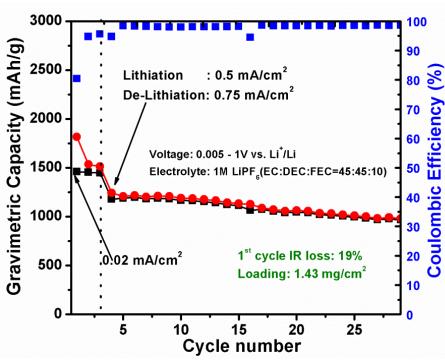


- > 1st Discharge capacity > 2890 mAh/g at 0.5 A/g current density
- ➤ IR loss: 27%, Coulombic Efficiency: 99.9%
- At 4 A/g (2.5C) current density, the capacity drops to only ~1500 mAh/g
- Capacity fade <0.05 % loss per cycle</p>
- Loading: 0.6 mg/cm²

Umicore-Si vs. h-SiNTs



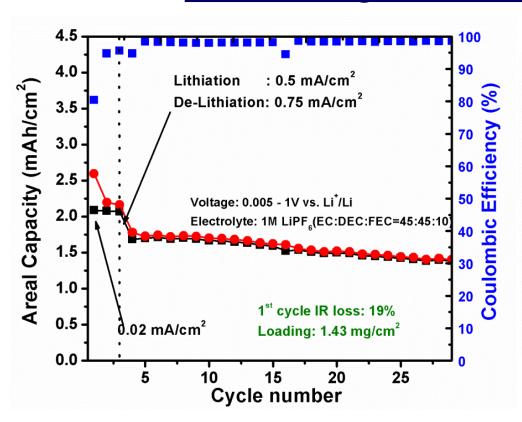


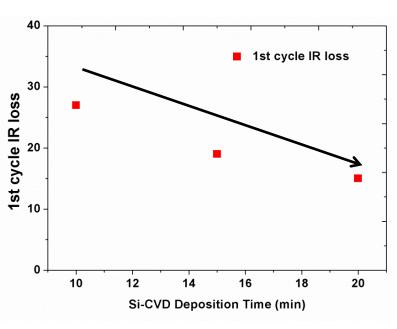


- Loading: 1.73 mg/cm²
- > 1st cycle IR loss: 15%
- Electrode composition: 50:25:25 (UMI-Si:binder: Super-P)
- Capacity calculated based on weight of the dry laminate
- ➤ Electrolyte: 1M LiPF₆ (EC:DEC:FEC=45:45:10)

- Loading: 1.43 mg/cm²
- 1st cycle IR loss: 19%
- Electrode composition: 50:25:25 (SiNTs:binder: Super-P)
- Capacity calculated based on weight of the dry laminate
- ➤ Electrolyte: 1M LiPF₆ (EC:DEC:FEC=45:45:10)

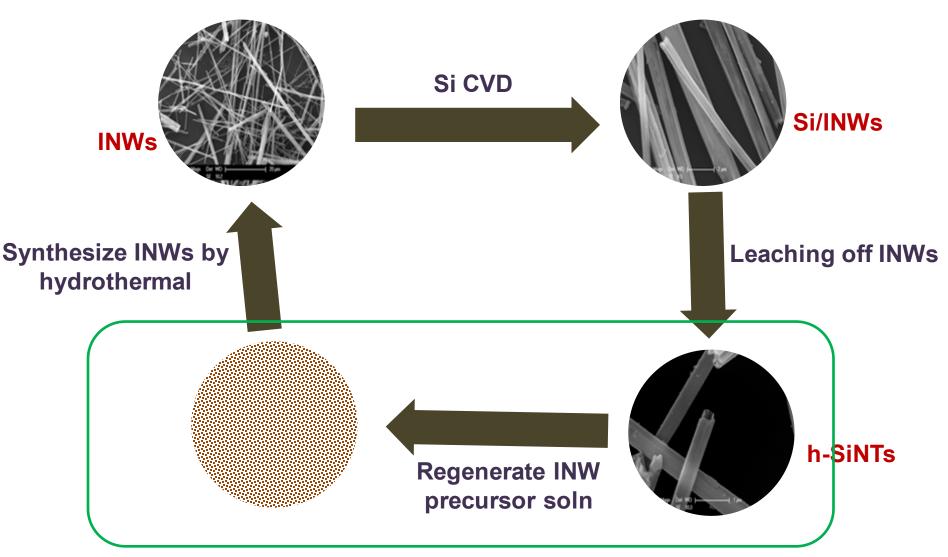
h-SiNTs: High Areal Capacity and FIR





- ➤ Loading: 1.43 mg/cm², Areal capacities ≥ 1.5 mAh/cm² meeting DOE-BATT guidelines have been achieved
- > IR loss: 19%, Columbic Efficiency: 99.0 %
- FIR loss decreases with the increase in the time of deposition of Si during CVD

Facile and Fully Recyclable Approach to h-SiNTs



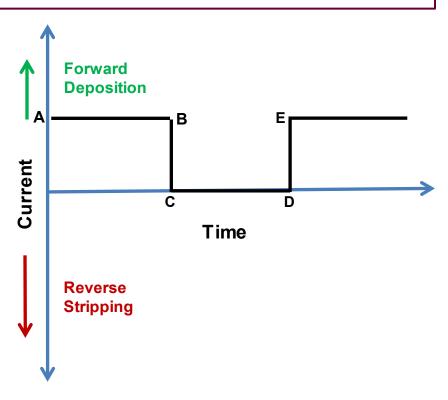
Amorphous Si (a-Si) Films: Pulsed Current Electrodeposition

Working Electrode: Cu foil

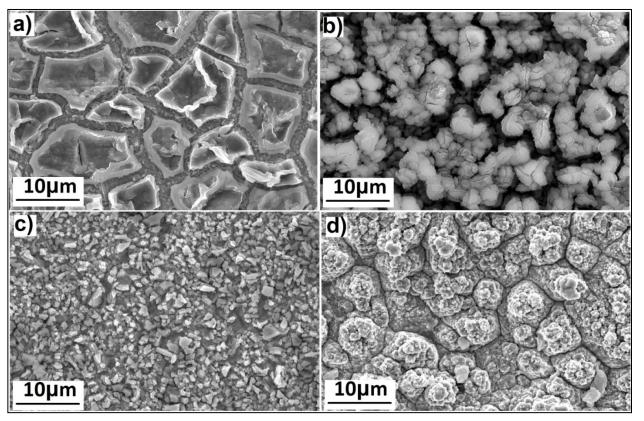
Counter and Reference electrode: Pt

Electrolyte: 0.5M SiCl₄ + 0.1M Tetrabutyl ammonium chloride in propylene carbonate

- Applied Current Density: -1mA/cm²
- > Deposition Time: 1hor 60mA-min/cm² charge
- Frequency of Deposition = 0Hz (DC), 500Hz, 1000Hz, 2000Hz, 3000Hz, 4000Hz, 5000Hz
- Duty Cycle = 50%
- > AB = ON Time
- > CD = OFF Time
- Frequency = 1/ (AB+CD)
- \rightarrow Duty Cycle = (100 x AB)/(AB+CD)
- ➢ Reduction of Si⁺⁴ ion takes place during On Time when the deposition current flows through the electrodeposition cell.
- During the Off Time there is no current flowing through the electrodeposition cell and hence, no deposition takes place.



Amorphous Si (a-Si) Films: Pulsed Current Electrodeposition

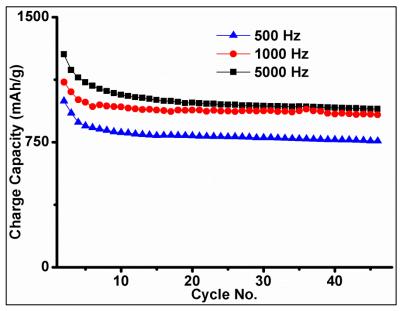


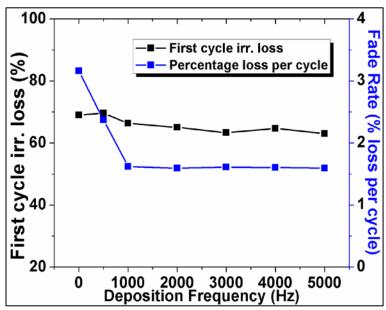
SEM images of electrodeposited amorphous Si films at different frequencies

- a) 0Hz (DC)
- b) 500Hz
- c) 1000Hz and
- d) 5000Hz

- ➤ Galvanostatic deposition (0 Hz) shows a mud-crack (island) morphology, the 500Hz deposition shows a cracked morphology with the islands consisting of agglomerated discrete particle deposits and the 1000Hz deposition shows a continuous thin layer comprised of Si particles.
- At higher frequency of deposition (2000Hz, 3000Hz, 4000Hz and 5000Hz) the deposited a-Si film is continuous without any major change in the morphology of the deposit. However, the particles contained in the thin film are smaller as compared to 500Hz and 1000Hz deposited films.
- > Inexpensive and simple method without use of any additives to change the morphology of deposition.

Amorphous Si (a-Si) Films: Pulsed Current Electrodeposition





Charge capacity of a-Si thin films deposited at 500Hz, 1000Hz and 5000Hz.

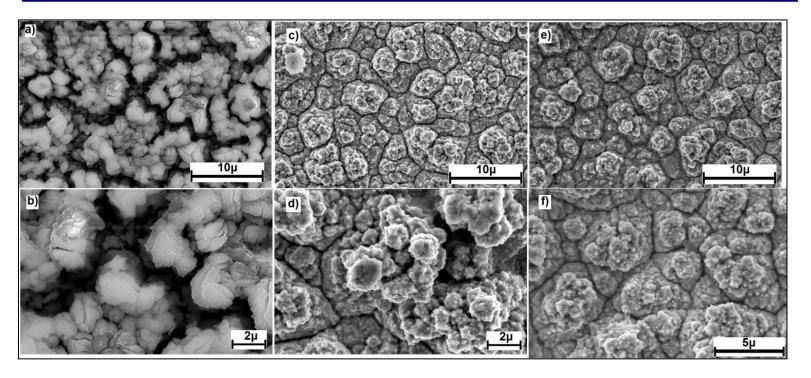
First cycle irreversible loss and Percentage loss per cycle vs Frequency of electrodeposition for a-Si films

Electrolyte: 1M LiPF₆ in EC:DEC=1:2 (v:v), No conductive additive or binders.

Current rate: 400 mA/g, (C/5 rate), Voltage: 0.02–1.2 V, Loading: 0.3-0.5 mg/cm²

- A significant part of charge capacity decreases in the first 10 cycles (~1.6% loss per cycle) of lithiation and delithiation for all the films following which there was minimal loss (~0.2% loss per cycle) in the charge capacity of the a-Si thin films.
- The capacity fade or the percentage loss of capacity per cycle (calculated for 10 cycles) indicates a decreasing trend with increase in the frequency of the deposition reaching a saturation value for higher frequencies.
- > Explore deposition and coating of conductive additives to reduce the FIR.

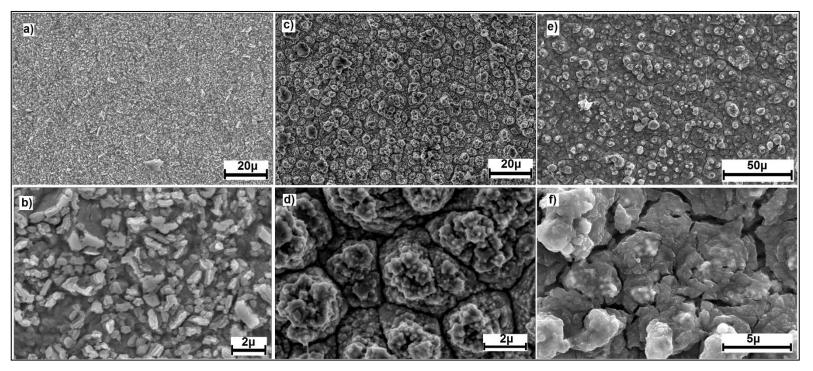
Amorphous Si (a-Si) Films: Pulsed Current Electrodeposition



SEM images of amorphous Si films electrodeposited at 500Hz a) and b) before cycling; c) and d) after 10; e) and f) after 50 cycles . a), c), e) at lower magnification and b), d), f) at higher magnification.

- As deposited Si film at 500Hz show a cracked morphology with the islands consisting of agglomerated discrete particle deposits.
- The particle morphology is transformed into cracked thin film morphology after first 10 cycles of lithiation and delithiation.
- No major change in the film morphology after 10 cycles and 50 cycles observed indicating stability of films upon lithiation and de-lithiation.

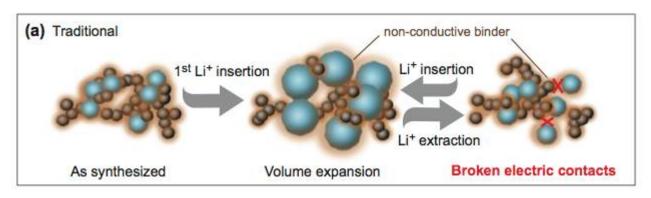
Amorphous Si (a-Si) Films: Pulsed Current Electrodeposition



SEM images of amorphous Si films electrodeposited at 1000Hz a) and b) before cycling; c) and d) after 10; e) and f) after 50 cycles . a), c), e) at lower magnification and b), d), f) at higher magnification.

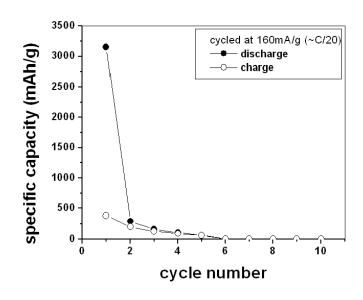
- The thin film develops cracks in initial 10 cycles which corresponds to the higher fade rate during the initial cycle.
- No major change in the film morphology after 10 cycles and 50 cycles indicating stability of films on lithiation and de-lithiation.
- Similar observation for Si thin films electrodeposited at 5000Hz frequency.

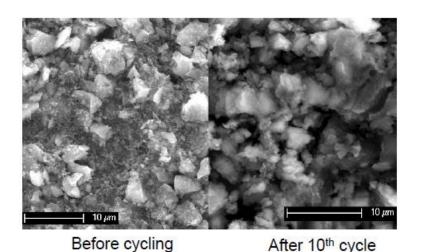
Problems with commercial binder: Failure of particles and binder



Pure Si: ~400% volume expansion



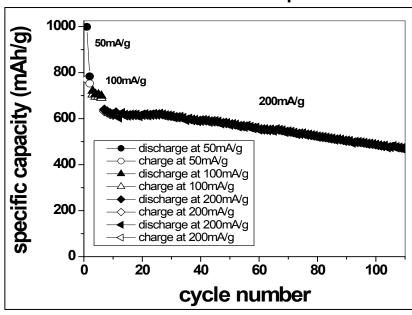


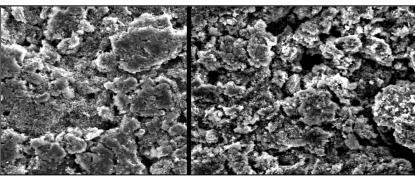


PVDF binder

Effect of Binder on the cyclability of Si/C composite anode (~600mAh/g)

Si/C composite electrode: 10wt.% PVDF binder





After cycling

Before cycling

Before cycling

Before cycling

¹H NMR spectra of PVDF in DMSO-d6. Spectrum at the bottom was collected before cycling and the spectrum at top was obtained after cycling. The broad resonances around 2.9 ppm correspond to the PVDF polymer. After cycling, the resonance corresponding to PVDF is not seen probably *due to degradation of the polymer.*

Loading ~2.5mg/cm² FIR at 50mA/g: ~20%

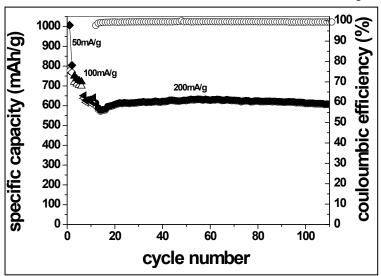
Cycled at ~200mA/g (C/3 rate), Potential window: 0.01V-1.2V,

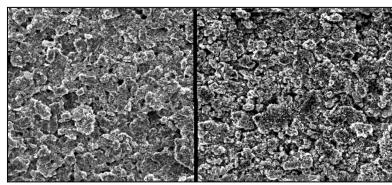
Reversible capacity at C/3 rate: ~600mAh/g, CE ~99.95%

Capacity fade: 0.2% per cycle for PVDF binder

Effect of Binder on the cyclability of Si/C composite anode (~600mAh/g)

Water soluble, Environmentally friendly, Cost effective Novel PP binder

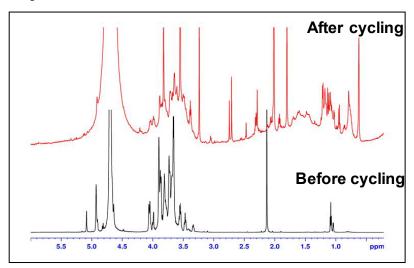




After cycling

Improved cyclability and mechanical integrity in comparison to PVDF

Before cycling



 1 H NMR spectra of PP in D_2O . Spectrum at the bottom was collected before cycling and the spectrum at top was obtained after cycling. The broad resonances in the region 3-4.2 ppm correspond to the PP polymer. **Even after cycling, the proton NMR shows structural integrity of PP.**

Loading ~2.5mg/cm²

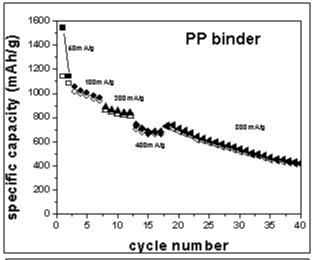
Cycled at ~200mA/g (C/3 rate), Potential window: 0.01V-1.2V

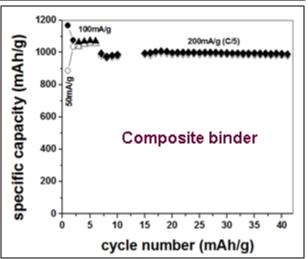
Reversible capacity at C/3 rate: ~600mAh/g

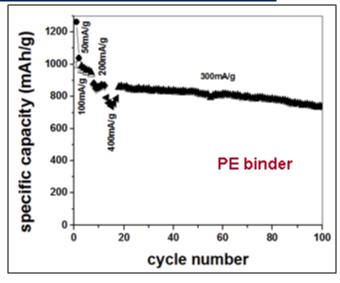
FIR at 50mA/g: ~20%, CE: 99.93%

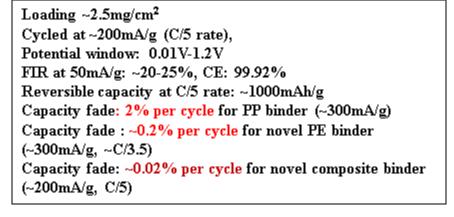
Capacity fade: ~0.04% per cycle for novel PP binder

Effect of Binder on the Cyclability of high capacity Si/C Composite (~1000mAh/g)









- PP binder not suitable for high capacity Si
- Novel PE and composite binder shows excellent cyclability of high capacity Si/C based electrode

Response to Reviewers Slide

Response to Reviewers

- Reviewer comments: High cost using CNTs and eBeam techniques
- Response/Action: We recognize that CVD of CNT is relatively expensive. In our recent approach, we have therefore demonstrated a low cost and scalable approach for generating hollow silicon nanotubes. These nanotubes are very promising in terms of achieving low first cycle irreversible loss (15-25%), high capacity (>2000 mAh/g) and good cyclability (fade rate 0.06 % loss/cycle for 400 cycles). The current approach using CVD to make amorphous Si is relatively inexpensive and is commonly used by Si device industries.
- We agree that using e-Beam to deposit the ICA on CNTs may not be economical, however alternative and more commonly used methods of CVD to form ICA are currently being explored.
- Reviewer comments: Low areal capacity of h-SiNTs
- Response/Action: Silicon nanotube electrodes with increased loading (>1.4 mg/cm²) have been fabricated showing higher areal capacity (~1.5-2.0 mAh/cm²).
- Reviewer comments: High FIR in high surface area Si
- Response/Action: We agree that high surface area Si exhibits high FIR. Correspondingly we have demonstrated a new high throughput h-SiNT approach that results in lowering the FIR to ~15-19%.

Response to Reviewers Slide

Response to Reviewers

- Reviewer comments: Impact of amorphous and nanocrystalline silicon on cycling
- Response/Action: From our studies, amorphous silicon obtained by CVD and electrodeposition exhibited better capacity retention (<0.05 % loss per cycle) compared to nanocrystalline silicon obtained by mechanical milling.
- Reviewer comments: Need to focus on fewer approaches
- Response/Action: From our studies, the hollow silicon nanotubes have exhibited better electrochemical performance in terms of achieving low first cycle irreversible loss (15-25%), high capacity (>2000 mAh/g) and good cyclability (fade rate 0.06 % loss/cycle for 400 cycles) compared to silicon obtained from other approaches. The approach is also scalable and recyclable possibly representing a low cost approach. Thus, our research has focused more on working with h-SiNTs to further improve areal capacity and decrease first cycle irreversible loss.
- Reviewer comments: Need to do post-mortem analysis of high strength binder
- Response/Action: Post-cycling analysis of the high strength binder has been conducted and reported in the current AMR review.

Response to Reviewers Slide

Response to Reviewers

- Reviewer comments: Need to achieve higher areal capacity (>5mAh/cm²)
- Response/Action: Compared to earlier work we have significantly increased the areal capacity to achieve ~1.5-2 mAh/cm² which is the recommendation by the DOE-BATT program for the Si anodes.
- Reviewer comments: Need more collaboration
- Response/Action: We are also collaborating with Carnegie Mellon University in performing nano-CT characterization of h-SiNTs to understand the structural changes after repeated cycling. Accordingly, a mechanical model is also being developed to support these findings. Additionally, we have collaborated with NETL, Morgantown on microwave synthesis and electrodeposition as well as X-ray photoelectron spectroscopy.

Collaboration Slide

Collaborations

Industries

Ford Motor Company

National Laboratory

- Dr. A. Manivannan, NETL
- Dr. Vincent Battaglia, LBNL

Other Universities

- Dr. Spandan Maiti, University of Pittsburgh
- Dr. Shawn Litster, Carnegie Mellon University
- Dr. Amit Acharya, Carnegie Mellon University
- Dr. Damodaran Krishnan, University of Pittsburgh

Remaining Challenges and Barriers

- Reduction of FIR below 15%
- Improve CE greater than 99.9%
- Improve the capacity fade rate to less than 0.01%loss/cycle over 3000 cycles
- Improve areal capacity greater than 2mAh/cm²

Future Work Slide

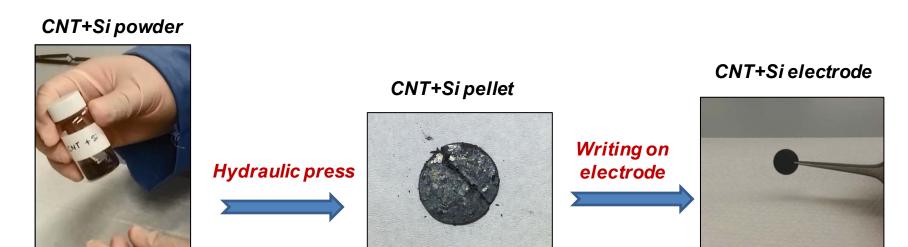
Future work

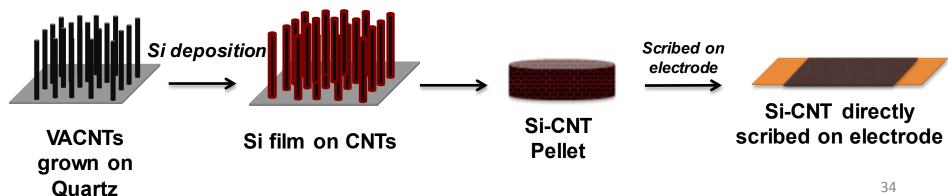
- Carbon coating on hollow silicon nanotubes using chemical vapor deposition to reduce the first cycle irreversible loss, improve the stability of interface and reduce the fade rate.
- Electro-less copper coating/deposition on the surface of hollow silicon nanotubes to improve the conductivity, rate capability and reduce FIR.
- Decrease the FIR in electrodeposited amorphous Si films by coating of carbon on the film.
- Improvement in the areal capacity of electrodeposited Si film by using stacked multilayered composite electrode of [a-Si/C/]_n.
- Electrodeposition of amorphous Si on carbon nanofibers to reduce the FIR, improve the interfacial energy and charge transfer kinetics.
- Improve the binder-silicon interfacial strength by functionalization and cross linking of the polymer binder.

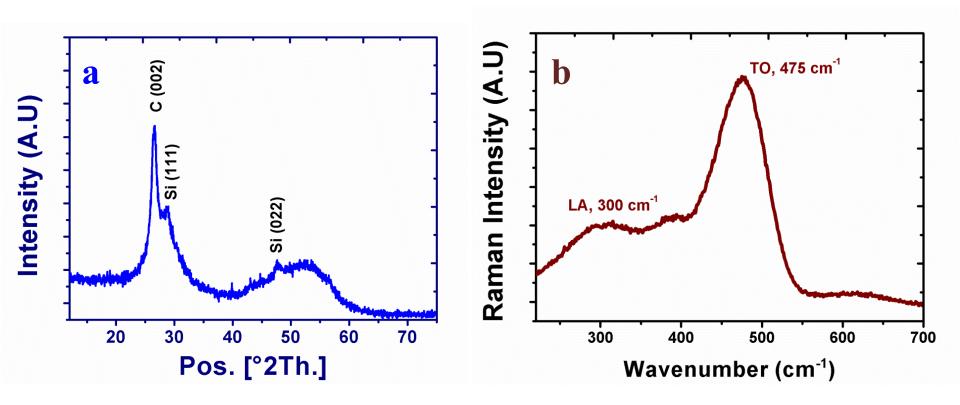
Summary Slide

Summary

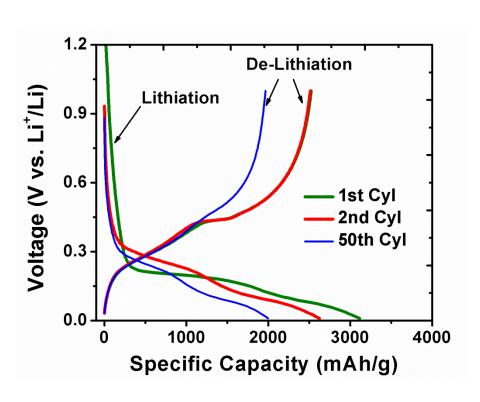
- ➤ Hollow Silicon nanostructures show 1000 mAh/g with good capacity retention (Fade rate=0.067 %loss/cycle) at the end of 400 cycles at 2A/g.
- ➤ **High areal capacity (≥1.5 mAh/cm²)** and increased loading (**1.4 mg/cm²**) have been achieved by increasing the deposition time of Si during the synthesis of hollow silicon nanotubes.
- ➤ The first cycle irreversible loss in **hollow silicon nanotubes was decreased to ~15%** with increase in the CVD-Si deposition time.
- ➤ Cycling results on Si/C composite with the identified **novel high strength PP, PE and** composite binder indicate **superior capacity retention** than **PVDF**.
- > Pulsed current electrodeposition resulted in uniform morphology of amorphous Si films at higher frequencies of deposition.
- ➤ Electrodeposited amorphous Si thin films show increase in stability with increase in pulsing frequency during electrodeposition.
- ➤ The Si films deposited at a pulsing cycle frequency of 5000Hz shows stable capacity of 850 mAh/g at 400mA/g at the end of 50cyles.

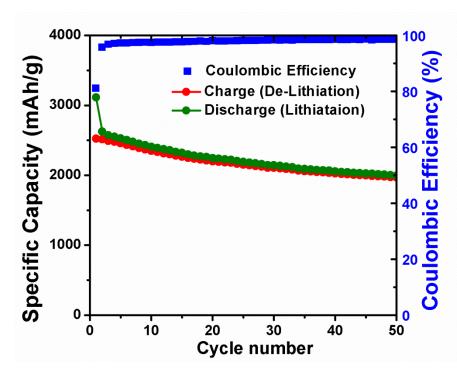




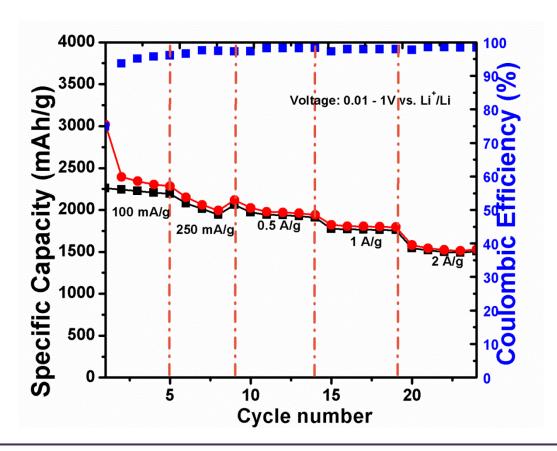


- > XRD shows the presence of graphitic (CNTs) and nc-Si/amorphous Si peaks
- > Raman spectra shows the presence of TO band for a-Si





- Current: 300 mA/g and Voltage: 0.01 to 1 V vs. Li⁺/Li
- 1st Discharge capacity: 3112 mAh/g, FIR= 19%
- ➤ Fade rate: 0.48%loss/cycle , Capacity retention of 76% after 50 cycles
- > IR loss: 19%, Coloumbic Efficiency: 98.5% Loading: 0.3-0.5 mg/cm²



- → 1st Discharge capacity → 3017 mAh/g at 0.1 A/g current density
- > IR loss: 22%, Coulombic Efficiency: 98%
- At 2 A/g current density, the capacity drops to only ~1700 mAh/g
- Loading: 0.4 mg/cm²